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# Microstructure and optical appearance of anodized friction stir processed Al - Metal oxide surface composites

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## Summary

Multiple-pass friction stir processing (FSP) was employed to impregnate Ti, Y and Ce oxide powders into the surface of an Aluminium alloy. The FSP processed surface composite was subsequently anodized with an aim to develop optical effects in the anodized layer owing to the presence of incorporated oxide particles which will influence the scattering of light. This paper presents the investigations on relation between microstructure of the FSP zone and optical appearance of the anodized layer due to incorporation of metal oxide particles and modification of the oxide particles due to the anodizing process. The effect of anodizing parameters on the optical appearance of the anodized surface was studied. Characterization was performed using FIB-SEM and TEM. The surface appearance was analysed using spectrophotometry technique which measures the diffuse and total reflectance of the surface. The appearance of the anodized surface changed from dark to bright upon increasing the anodizing voltage. Particles in the FSP zone were partially or completely modified during the anodizing process and modified the morphology of the surrounding anodized Al matrix which has a clear influence on the mechanism of light interaction like scattering and absorption from the anodized surface.

## 1 Introduction

Aluminium alloys are widely used in aerospace, automobile and architectural applications due to their high mechanical strength to weight ratio. Anodizing of Al improves its decorative appearance and resistance to corrosion and wear [1]. Sulphuric acid anodizing (SAA) transforms the Al surface to a clear and transparent anodic oxide which comprises a self-organized hexagonal porous structure (20-30 nm pore diameter) [2] [3]. This structure can be later dyed using capillary effect and sealed in boiling water to impart colours to the anodized surface [4]. A wide range of colours, including black have been produced over the years but achieving a white glossy anodized Al surface is difficult. This is because white appearance is generated by scattering of light by particles that are bigger than the pores while colours are generated by selective absorption of particular wavelengths by dye molecules that are smaller than the pores [5] [6].

White anodized Al is sought for applications in the aerospace and architectural industry where a low solar absorptance is preferred to prevent temperature rise and related thermal expansion of structural components. Also, it is of great interest for aesthetic/decorative purposes in the architectural industry for building facades, window profiles etc. White anodized Al has been reported earlier using a mixture of electrolytes, but the reflectance from these surfaces is not very high [7] [8]. Alternate processes based on Plasma Electrolytic Oxidation (PEO) and Micro Arc Oxidation (MAO), which are commercially available reported grey to white anodized surfaces. However the surfaces generated by these methods are low in gloss as they have a high surface roughness [9] [10] [11].

Glossy white anodized surface requires scattering of incident light within the anodic layer and also generate a surface gloss due to specular reflectance from a smooth surface without any absorption in the visible wavelength region [12] [13] [14]. One approach for achieving this is to mimic the optical scattering phenomenon from white paints which contain a pigment in a polymer matrix. The pigments used should have a high refractive index difference with the surrounding polymer matrix and enable very efficient scattering. Similar scattering effects can be achieved using metal oxides (based on Ti, Y and Ce) in anodic alumina which has a refractive index similar to polymer matrix of paints [15] [16]. To obtain such a structure on the anodized Al surface, metal oxide particles need to be incorporated into the Al matrix prior to anodizing and the obtained composite be later anodized to reveal these particles in a transparent anodic alumina matrix (similar to paints).

Incorporation of metal oxides particles into metallic matrices has been of great interest due to the enhancement in mechanical properties of the obtained composites by particle reinforcement. Various techniques have been employed to prepare many composite systems [17] [18] [19] [20] [21] [22]. Friction stir processing (FSP) [23] is one such technique that has been extensively used for preparation of composites [24] [25] [26] [27] [28]. However, use of this technique to obtain composite surfaces for white anodizing of Al has not yet been attempted.

In the present work we present the initial findings on use of metal oxides incorporation into Al matrix for white anodizing. The effect of anodizing parameters on the obtained optical appearance is studied. Transmission electron microscopy (TEM) was used to investigate the structure and morphology of the anodized composites. Surface appearance was characterized using reflectance spectroscopy and the obtained results are explained in terms of microstructural and morphological features of the anodic layer.

## **2 Experimental**

Aluminium substrates with dimensions 200 mm x 60 mm x 6 mm were obtained in rolled condition. Commercial powders of  $\text{TiO}_2$  (300 nm),  $\text{Y}_2\text{O}_3$  (0.5-1  $\mu\text{m}$ ) and  $\text{CeO}_2$  (200 nm) were used. Friction stir processing was performed using a Hermle milling machine equipped with a steel tool having 20 mm shoulder diameter, 1.5 mm pin length with a M6 thread and three flats. A groove 0.5 mm deep, 10 mm wide and 180

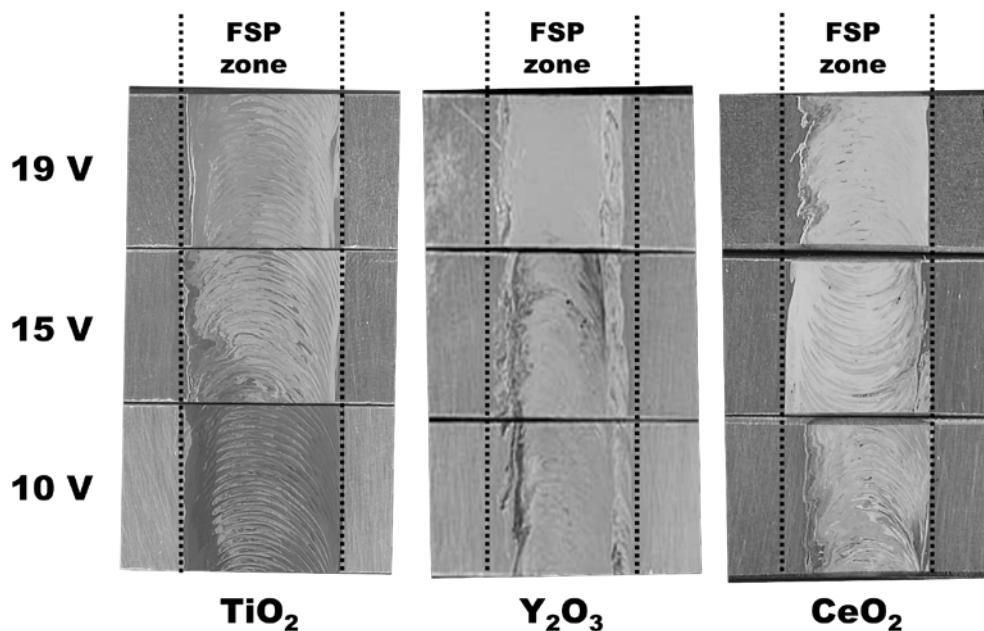
mm long in the substrates was filled with the powders. The filled substrates were then covered by the same Al sheet rolled down to a thickness of 0.25 mm to prevent loss of powders during the initial FSP pass.

The processed composite surfaces were mechanically polished to a mirror finish and subsequently degreased in a mild alkaline solution. Desmutting was performed by immersing in dilute  $\text{HNO}_3$  followed by demineralised water rinsing. Anodizing was carried out in a 20 wt.% sulphuric acid bath maintained at 18 °C. Three different anodizing voltages of 10 V, 15 V, and 19 V were used. After anodizing, the samples were rinsed with demineralized water. Sealing of the anodized layer was performed in boiling water.

Surface appearance of the processed composites after anodizing was analysed using an integrating sphere-spectrometer setup. The samples were illuminated with light from a Deuterium-Tungsten halogen light source. Reflected light from the samples was collected and analysed for diffuse and total reflectance using a spectrometer. The spectrometer was calibrated using NIST standards. Transmission electron microscopy analysis was carried out on the sample cross section in the anodized as well as non-anodized regions using a TEM (Model Tecnai G2 20). The lamellas for TEM were prepared using FIB-SEM in situ-lift out (Model Quanta 200 3D DualBeam, FEI) and further thinned for electron transparency in a FIB-SEM (Helios Nanolab DualBeam, FEI).

### 3 Results

#### 3.1 Visual Appearance

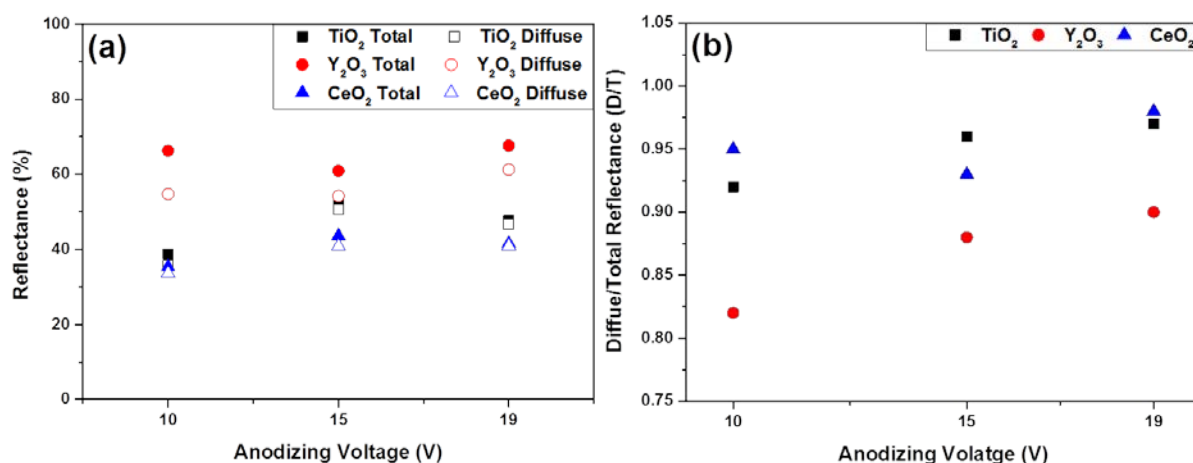


**Figure 1:** Visual appearance of the friction stir processed samples with different powders after sulphuric acid anodizing at different voltages.

The visual appearance of the FSP samples after anodizing is shown in Figure 1. The FSP zone shows a different appearance for all three powders when compared to the adjacent unprocessed Al. The processed zone can be clearly identified (region between dotted lines) as it shows macroscopic semi-circular striations. For all the three powders types used, the anodized appearance shifts from dark to greyish white as the anodizing voltage is increased from 10 V to 19 V. This effect is most prominent in the case of surface containing  $\text{TiO}_2$  powders where there is a clear difference between the surfaces anodized at 10 V and 15 V.

### 3.2 Reflectance Spectroscopy

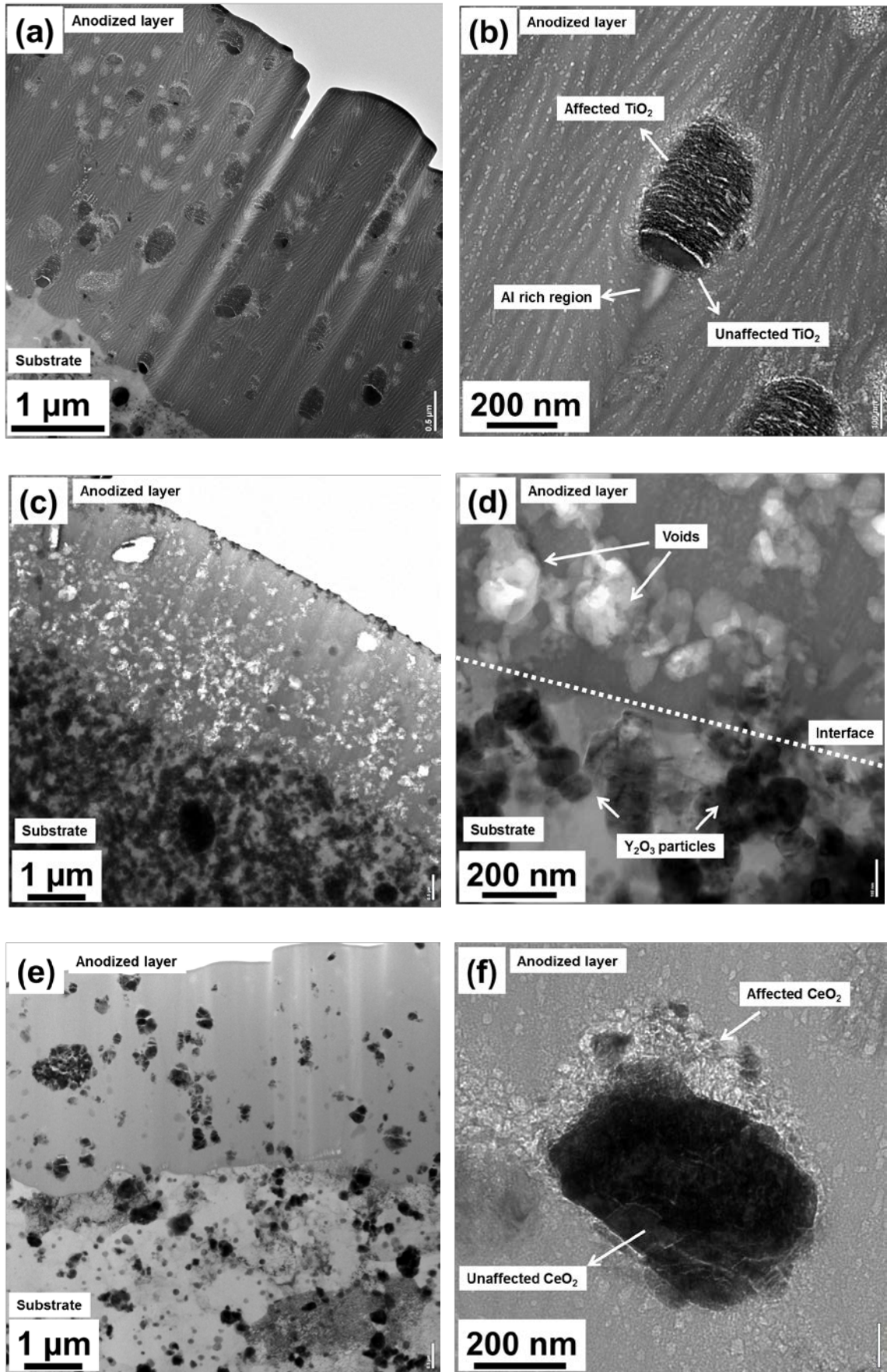
The reflectance values (at 555 nm) obtained from the spectrophotometry are presented in Figure 2(a). It can be seen that the total reflectance of the anodized surface increases from anodizing at 10 V to 15 V and then slightly reduces at 19 V for  $\text{TiO}_2$  and  $\text{CeO}_2$ . However, for samples containing  $\text{Y}_2\text{O}_3$ , the total reflectance is lower at 15 V anodizing when compared to the 10 V and 19 V anodizing. The diffuse to total reflectance ratio which is a measure of how well the surface scatters light is shown in Figure 2 (b). It can be observed that the diffuse reflectance component for the  $\text{Y}_2\text{O}_3$  containing surfaces is lower than that for  $\text{TiO}_2$  and  $\text{CeO}_2$  even though their total reflectance value is lower.



**Figure 2:** (a) Total and diffuse reflectance values (wavelength~555 nm) and (b) Diffuse to Total reflectance (D/T) ratio obtained from the FSP surfaces after sulphuric acid anodizing at different voltages.

### 3.3 Transmission Electron Microscopy

The anodized layer on sample containing  $\text{TiO}_2$  which is anodized at 19 V (Figure 3(a)) shows different morphological features for the  $\text{TiO}_2$  particles. In this case, the particles present in the anodized layer are fully or partially transformed. Typical features of the  $\text{TiO}_2$  particle in Figure 3(b) show that the particle is partially affected (top region of the particle) by the anodizing process. Also, the picture shows a bright region below the  $\text{TiO}_2$  particle. Elemental analysis of the bright regions using EDS show presence of higher contents of Al compared to surrounding regions which showed Al, Ti and O. The anodized layer on the sample containing  $\text{Y}_2\text{O}_3$  particles is shown in Figure 3(c).



**Figure 3:** TEM bright field image showing anodized layer cross section of FSP and anodized samples with (a), (b) TiO<sub>2</sub>, 19 V, (c), (d) Y<sub>2</sub>O<sub>3</sub>, 10 V and (e), (f) CeO<sub>2</sub> 10 V.



Unlike the  $\text{TiO}_2$  containing sample, the  $\text{Y}_2\text{O}_3$  particles are not present in the anodized layer. The anodized layer shows large number of voids, although the FSP substrate shows good distribution of  $\text{Y}_2\text{O}_3$  particles (Figure 3(d)). The voids are expected to be the result of expelled  $\text{Y}_2\text{O}_3$  particles during the anodizing process. For the samples containing  $\text{CeO}_2$ , anodizing at 10 V showed similar morphological features as for the  $\text{TiO}_2$  particles (Figure 3(e)). One of the  $\text{CeO}_2$  particles shown in Figure 3(f) appears affected (top region of the particle) by the anodizing process. However, regions of high Al content like those observed beneath the  $\text{TiO}_2$  particles have not been observed in the anodized layer of  $\text{CeO}_2$  containing samples.

## 4 Discussion

Friction stir processing of Al substrates with metal oxide powders resulted in a surface composite with good distribution of particles in the processed zone. Anodizing of these composite surfaces visually revealed macroscopic inhomogeneity in the processed zone like semi-circular striations (Figure 1). These striations are caused by the forward movement of the tool that generates a trail behind it. Overall distribution of particles in the FSP zone is uniform without any significant agglomeration (Figure 3). In all the cases, upon visual observation the surface appearance changed from dark to greyish white with increasing anodizing voltage. Reflectance spectroscopy data (Figure 2) measured by the integrating sphere setup showed that the reflectance values are highest for the  $\text{Y}_2\text{O}_3$  containing surfaces when compared to the  $\text{TiO}_2$  and  $\text{CeO}_2$  containing surfaces irrespective of the anodizing voltage used. For anodized surfaces containing  $\text{TiO}_2$  and  $\text{CeO}_2$  the reflectance increased from 10 V to 15 V anodizing and later decreased from 15 V to 19 V anodizing. However for the  $\text{Y}_2\text{O}_3$  containing samples, the reflectance was lowest for anodizing at 15 V. The TEM images shown in Figure 3 reveal that the morphology of the anodic layer and particles is different for different powders used. For  $\text{Y}_2\text{O}_3$  powders the anodized layer showed very little presence of the particles. Surfaces containing  $\text{TiO}_2$  and  $\text{CeO}_2$  showed partially affected particles in the anodic layer. Also, un-anodized Al rich regions were observed beneath the  $\text{TiO}_2$  particles in the anodized layer.

The difference in reflectance values measured from the anodized surfaces containing different powders is a manifestation of various factors like the refractive index of the powders, the distribution and concentration of the powders, the roughness of the surface and the interface between anodized layer and substrate, morphology of the anodized layer as well as of the powder particles [5] [6]. High refractive index particles in a visibly transparent medium scatter light and increase the diffuse reflectance. The increased scattering is due to the refractive index difference between the particle and the surrounding medium. In the present case, the metal oxide particles have a higher refractive index when compared to anodic alumina ( $n=1.6-1.7$ ) [29] [30] and hence result in a high diffuse reflectance value. However, the total reflectance value measured is only 40-60% of the incident light intensity. The loss of intensity can be explained by the morphological features observed in the anodic layer. In the case of anodized layer with  $\text{TiO}_2$ , regions of high Al content observed beneath the particles act as absorption centres for light. Anodic alumina is a transparent medium under visible light, but Al as a metal has a very high optical extinction coefficient. This coupled with the sub-micron size of the metallic Al region leads to an effective extinction

of light and hence the reduced loss of reflected intensity [31] [32] [33]. The presence of these metallic Al regions in anodic alumina depends on the anodizing voltage as the oxidation power of the process increases with anodizing voltage [34] [35]. At lower anodizing voltages the oxidative power is not sufficient to fully anodize the Al beneath the insulating  $\text{TiO}_2$  particles owing to the current field distribution [36]. Hence, an increased amount of such metallic Al in anodized layer results in higher absorption of light and thus the reduced reflectance values. As the anodizing voltage increases, it is assumed that the Al surrounding the  $\text{TiO}_2$  particle gets completely anodized increasing the reflectance. The  $\text{Y}_2\text{O}_3$  containing anodized surfaces show no such Al rich regions and also have a higher reflectance values. This is due to the absence of any insulating particles in the anodized layer as seen in Figure 3(c). Also, as the particles have been removed from the matrix during the anodizing process, the diffuse reflectance obtained in this case is due to the scattering from voids rather than the particles themselves. A lower diffuse reflectance component observed for the  $\text{Y}_2\text{O}_3$  containing surfaces (Figure 3(b)) is due to the fact that the incident light is now reflected from the anodized layer – metal substrate interface, which is similar to the reflection from a smooth metal surface which appears glossy (specular). The phenomenon of transformation of crystalline  $\text{TiO}_2$  and  $\text{CeO}_2$  particles to amorphous phase and also the removal of  $\text{Y}_2\text{O}_3$  particles after anodizing of these composites is yet to be understood and requires more detailed analysis.

Refractive index of  $\text{TiO}_2$  ( $n=2.6-2.9$ ) [37] is higher than that of  $\text{CeO}_2$  ( $n=2.2-2.4$ ) [38] and hence the scattering efficiency of the anodized Al- $\text{TiO}_2$  system would be better than that of anodized Al- $\text{CeO}_2$  system. However, from the reflectance values, only slight difference was observed at a given voltage. This could be attributed to the transformation of  $\text{TiO}_2$  to amorphous phase in the anodic alumina with a reduced refractive index ( $n=2.42$ ) [39] [40]. A white glossy anodized Al surface would have a total reflectance of 80-90% with a very high diffuse reflectance component. The values obtained for such surfaces using metal oxide incorporation into Al matrix before anodizing have been shown to be max. 50%. Use of  $\text{Y}_2\text{O}_3$  gives higher reflectance value, but the voids generated reduce the mechanical properties of the anodic alumina layer. When comparing between  $\text{TiO}_2$  and  $\text{CeO}_2$ , it has been observed that the reflectance values do not differ considerably. However high values of reflectance would be achieved if higher particle concentrations are used and the crystalline nature of the oxide particles is retained after anodizing.

## 5 Conclusions

- Friction stir processing was employed to prepare Al with Ti, Y and Ce oxide surface composites with little or no agglomerations of particles.
- Sulphuric acid anodizing of the prepared surface composites showed an increase in surface brightness with increasing anodizing voltage.
- High resolution TEM analysis show that the anodizing process transformed the  $\text{TiO}_2$  and  $\text{CeO}_2$  particles to amorphous state, while the  $\text{Y}_2\text{O}_3$  particles were removed from the Al matrix during anodizing.
- Anodizing at lower voltages showed the presence of un-anodized crystalline Al regions below the  $\text{TiO}_2$  particles.



- Presence of metallic Al in the anodic alumina along with the reduced refractive index of TiO<sub>2</sub> and CeO<sub>2</sub> particles resulted in reduced reflectance of anodized surface.
- The Y<sub>2</sub>O<sub>3</sub> containing surfaces showed higher reflectance due to scattering from the voids in the anodic layer and reflection from the anodic layer-metal substrate interface.

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